Predicting trace metal solubility and fractionation in urban soils from isotopic exchangeability.

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ABSTRACT

Metal-salt amended soils (MA, n = 23), and historically-contaminated urban soils from two English cities (Urban, n = 50), were investigated to assess the effects of soil properties and contaminant source on metal lability and solubility. A stable isotope dilution method, with and without a resin purification step, was used to measure the lability of Cd, Cu, Ni, Pb and Zn. For all five metals in MA soils, lability (%E-values) could be reasonably well predicted from soil pH value with a simple logistic equation. However, there was evidence of continuing time-dependent fixation of Cd and Zn in the MA soils, following more than a decade of storage under air-dried conditions, mainly in high pH soils. All five metals in MA soils remained much more labile than in Urban soils, strongly indicating an effect of contaminant source on metal lability in the latter. Metal solubility was predicted for both sets of soil by the geochemical speciation model WHAM-VII, using E-values as an input variable. For soils with low metal solution concentrations, over-estimation of Cd, Ni and Zn solubility was associated with binding to the Fe oxide fraction while accurate prediction of Cu solubility was dependent on humic acid content. Lead solubility was most poorly described, especially in the Urban soils. Generally, slightly poorer estimation of metal solubility was observed in Urban soils, possibly due to a greater incidence of high pH values. The use of isotopically exchangeable metal to predict solubility is appropriate both for historically contaminated soils and where amendment with soluble forms of metal is used, as in toxicological trials. However, the major limitation to predicting solubility may lie with the accuracy of model input variables such as humic acid and Fe oxide contents where there is often a reliance on relatively crude analytical estimations of these variables.

Capsule:

Trace metal reactivity in urban soils depends on both soil properties and the original source material; the WHAM geochemical model predicts solubility using isotopically exchangeable metal as an input.

1. INTRODUCTION

Accurate assessment of risk from heavy metal contamination of the environment requires consideration of metal 'reactivity' or 'lability' in soils (Fairbrother et al., 1999; Lock and Janssen, 2001). Published literature (Degryse et al., 2004, Tack, 2010, Hammer et al., 2006) generally suggests that the lability of trace metals in soils is the net result of three factors: (i) soil properties, including soil physicochemical characteristics such as pH (e.g. McBride et al., 2006; Bonten et al., 2008) and redox potential (Borch et al., 2010) and the proportions of soil constituents such as Fe/Mn hydroxide and organic matter present (Tipping et al., 2003; Rodrigues et al., 2010); (ii) metal sources, which may vary greatly in their intrinsic metal lability (e.g. Atkinson et al., 2011; Mao et al., 2014) and (iii) soil-metal contact time, because there is a time-dependency to both metal fixation in soils (e.g. Tye et al., 2003; Ma et al., 2006b) and the release of trace metals from contaminant sources in soils (Kaste et al., 2006; Atkinson et al., 2011). Generally, low metal lability is more likely in soils with high pH values and following long contact times. Recent studies have focused on the concentrations and origins of heavy metals in the urban environment (Manta et al., 2002; Cheng et al., 2014; Wei and Yang, 2010), but the effects on lability arising from characteristics of the original contaminant source are usually difficult to assess (Mao et al., 2014).

A range of techniques have been developed to measure the lability of trace element fractions in soils, among which isotope dilution is perhaps the most appropriate method (Degryse et al., 2009). This approach defines an amount of metal, distributed between the solution and solid phases, which is isotopically exchangeable, known as the E-value or M_E (Smolders et al., 1999; Young et al., 2000). Measurement is achieved by adding a small 'spike' of an enriched isotope of the analyte of interest into a pre-equilibrated soil suspension and measuring the isotopic abundance of the spike isotope in the separated solution phase. The extent to which the spike isotope has been able to mix with the indigenous soil metal quantifies the 'isotopically exchangeable' metal pool in the soil. The method has been modified to correct for the presence of non-labile metal in sub-micron colloidal particles (SCP-metal) by adding a resin purification step (Lombi et al., 2003). E-values can then be used as input variables to geochemical speciation models, such as WHAM (Windermere Humic Aqueous Model, Tipping et al., 2003) to predict metal fractionation and speciation in the solid and solution phases of soils respectively (Tipping et al., 2003; Shi et al., 2008; Almas et al., 2007; Buekers et al., 2008b; Marzouk et al., 2013b).

The primary aims of this study were to investigate how trace metal *lability* and *solubility* are affected by (i) soil properties, (ii) ageing and (iii) variable contamination sources in urban soils. To achieve this, objectives focussed on determination of the isotopically exchangeable fractions of Cd, Cu, Ni, Pb and Zn (M_E) in two distinct sets of soil samples. These included (i) soils, chosen for their range of land uses and soil properties, that had been incubated with metal nitrate salts (Cd, Cu, Ni, Pb and Zn) for several years and (ii) urban contaminated soils, from Nottingham and Wolverhampton (UK), chosen for their range of metal contaminant concentrations and sources. To reveal the effect of contaminant source, the 'lability' of soils from the two datasets were compared by normalising values of $\%M_E$ against soil pH;

logistical models for describing metal lability with pH were parameterised. Secondary objectives included: (i) testing for non-labile SCP-metal (<0.22 μm) by comparing values of M_E with equivalent values following a resin cleaning procedure (M_{Er}); (ii) testing for metal *fixation* in air dried soil stored for more than a decade, (iii) comparing a sequential fractionation scheme with fractionation by isotopic exchangeability and (iv) assessing the performance of the geochemical model, WHAM VII, to predict Cd, Cu, Ni, Pb and Zn solubility in both sets of soils.

2. MATERIAL AND METHODS

2.1 Soil sampling

Two sets of soils were used in this study. The first set comprised 23 metal-amended topsoils (MA soils), from sites with contrasting land uses and parent material, to provide a wide range of soil properties (pH, soil organic matter, mineral (hydr)oxides content and texture). These soils were collected for a previous study of trace metal fixation and solubility (Tye et al., 2003; Tye et al., 2004) and had been amended with metal nitrate salts to the limits prescribed by the UK Sludge Regulations (MAFF, 1993) (Cd = 3, Cu = 135, Ni = 75, Pb = 300 and Zn = 300 mg kg^{-1}) before being incubated at 16°C and 80% field capacity (FC) for ~3 years (Tye et al., 2003), air-dried, and then stored for ~12 years prior to the current study. The second set (Urban soils) consisted of 50 topsoils collected in the cities of Wolverhampton (WV) and Nottingham (NG), UK. Site selection included consideration of historical and recent industrial and domestic land use and locations included brownfield sites, rail transport sidings, urban roadsides, waste disposal facilities, recreational areas, gardens, urban nature reserves and woodland and parkland areas. Data relating to these soils has been published previously in an investigation of metal speciation and bioavailability in risk assessment (Thornton et al., 2008; Hough et al., 2005).

2.2 Soil characterization

Some of the soil properties originally determined were re-measured to identify changes during storage and to provide a more complete input dataset for subsequent modelling (Section 2.6). Soil pH was measured on suspensions (1 g soil: 30 mL of 0.01 M $Ca(NO_3)_2$) using a pH meter with combined Ag/AgCl glass electrode (Model pH 209, HANNA Instruments, Bedford, UK). Total organic matter content was estimated using a LECO combustion analyser (Tye et al., 2003) for MA soils. For Urban soils total organic matter content was calculated from the difference between total soil carbon (SC) content measured using an Elemental Analyser (CE Instruments model Flash EA1112) and calibrated using a range of certified soils, and carbonate content determined by manometric assay using the Collins' calcimeter method (Piper, 1954). Alkaline extraction was used to determine humic acid (HA) and fulvic acid (FA) content in all soils. Organic carbon content in HA and FA was measured using a Shimadzu TOC-Vcp analyser. Clay content (%) was estimated from the soil texture classification provided by Tye et al. (2003) for MA soils. Iron, Al and Mn oxide concentrations were determined following extraction with a mixture of sodium dithionite, sodium citrate and sodium bicarbonate (DCB extraction,

Anschutz et al., 1998). Total Cd, Cu, Ni, Pb and Zn concentrations in soil were determined following digestion of 200 mg of finely ground soil with HF (40% AR), HNO_3 (70% TAG), $HClO_4$ (70% AR) and 2.5 mL H_2O in a block digester (Model A3, Analysco Ltd, Chipping Norton, UK). Iron, Al and Mn in DCB extractants and trace metals in acid digests were analysed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Thermo-Fisher Scientific X-Series^{II}) operating in 'collision cell mode' (7% hydrogen in helium) to reduce polyatomic interferences.

2.3 Cadmium, Cu, Ni, Zn, and Pb lability measured by isotopic dilution (E-value)

Sample preparation

The stable isotopic dilution method used in this study was adapted from Atkinson et al. (2011). Soils were pre-equilibrated in 0.01 M $Ca(NO_3)_2$ (1 g: 30 mL) on an end-over-end shaker for 3 days; 4 suspensions were made for each soil. An aliquot (0.4 mL) of enriched stable isotope stock solution (ISOFLEX, San Francisco CA, USA) in ~2% HNO_3, with known isotopic abundances (IA) for ^{108}Cd (IA = 69.7%), ^{65}Cu (IA = 99.0%), ^{62}Ni (IA = 98.2%), ^{204}Pb (IA = 98.8%) and ^{70}Zn (IA = 92.7%) was added to two of the suspensions and the other two were used as control samples to derive the natural isotopic abundance of the labile metal. The spike isotopes used were, with the exception of ^{65}Cu, chosen because they have relatively low natural isotopic abundance (De Bievre and Barnes, 1985). Therefore, only a small addition to the system was required to produce a significant increase in IA from the background level. To reduce the number of individual operations and to avoid adding different amounts of isotopes to each soil, the samples were classified into several groups according to their soil metal content. The level of isotope tracer to be added was determined from the highest concentration of metal in each group to ensure that the difference in isotopic ratio between the spiked and un-spiked samples was at least 20 %. After spiking, the suspensions were shaken for a further 3 days; the solution and solid phases were then separated by centrifugation (2200 g) and then filtration (< 0.2 μm). For several Urban soils, where the native and/or spike metal concentrations in 0.01 M $Ca(NO_3)_2$ suspension were judged to be too low to provide reliable isotopic ratios (Midwood, 2007), a suspending solution of 1×10^{-5} M EDTA was used to shift the labile metal equilibrium in favour of the soil solution while presenting minimal risk of mobilizing non-labile metal, as shown by Atkinson et al., (2011) and Nazif et al., (2015).

ICP-MS settings for measuring isotopic abundances and calculation of E-value

Isotopic ratios in supernatant solutions were measured by ICP-MS in 'collision cell with kinetic energy discrimination' (CCT-KED) mode to avoid interference from the chlorine dimer (^{35}Cl-^{35}Cl), and other polyatomic species, on ^{70}Zn (Malinovsky et al., 2005; Stenberg et al., 2004). Quadrupole dwell times were short to reduce plasma flicker: ^{108}Cd (10 ms), ^{111}Cd (2.5 ms), ^{63}Cu (2.5 ms), ^{65}Cu (10 ms), ^{60}Ni (2.5 ms), ^{62}Ni (10 ms), ^{204}Pb (10 ms), ^{206}Pb (2.5 ms), ^{207}Pb (2.5 ms), ^{208}Pb (2.5 ms), ^{66}Zn (2.5 ms) and ^{70}Zn (10 ms). The isotopes ^{59}Co, ^{107}Ag and ^{202}Hg were also measured, as quadrupole settle points (Marzouk et al., 2013a). It is well known that the relative abundance of Pb isotopes varies according to the sources of Pb present in the soil (Komarek et al., 2008). Therefore, instead of relying on assumed

relative abundances of naturally occurring isotopes, the apparent isotopic ratio in un-spiked samples (blanks) was also determined for all five elements. To avoid the electron multiplier detector tripping to analogue mode, all the sample solutions were diluted appropriately.

A source of error when analysing stable isotopes is mass discrimination: isotopes with greater mass are measured by ICP-MS with greater sensitivity and so the measured ratio of CPS for two isotopes is not equal to their true isotopic ratio. External mass discrimination correction was therefore applied using a certified isotopic standard reference material (NIST, SRM 981) for Pb and a mix of single ICP-MS calibration standards for Cd, Cu, Ni, and Zn. The mixed standard (25 µg L^{-1}) was used to calculate a correction factor (K-Factor) (**Eq. 1**):

$$K - factor = \frac{IR}{CR} \quad (1)$$

where IR and CR are the true isotopic ratio and the measured ratio of CPS for the isotopic standard respectively. For individual samples, the K-factor for each isotopic ratio (e.g. $^{204}Pb/^{208}Pb$, $^{206}Pb/^{208}Pb$, $^{207}Pb/^{208}Pb$) was estimated by linear interpolation between the K-factor measured for standards run at intervals of eight samples.

Concentrations of isotopically exchangeable metal (M_E; mg kg^{-1}) were calculated for Cd, Cu, Ni, Pb and Zn from **Eq. 2** adapted from Gabler et al. (1999):

$$M_E = \left(\frac{Am_{Msoil}}{W}\right)\left(\frac{C_{spk}V_{spk}}{Am_{Mspk}}\right)\left(\frac{^{spk}IA_{spike} - {}^{bg}IA_{spike}\,R_{ss}}{{}^{bg}IA_{soil}R_{ss} - {}^{spk}IA_{soil}}\right) \quad (2)$$

where Am_{Msoil} and Am_{Mspk} are the average atomic masses of Cd, Cu, Ni, Pb or Zn in the soils and the spike isotope solution respectively, W is the weight of the soil (kg), C_{spk} is the gravimetric concentration of the metal in the spike solution, V_{spk} is the volume of spike added (L), IA is the isotopic abundance and R_{ss} is the ratio of isotopic abundances, spiked (spk): background (bg), for the two isotopes in the spiked soil solution. For comparative purposes, lability is often expressed as a percentage of the total metal content of the soil (%M_E)

A 'resin purification' test for the presence of non-labile metal in suspended colloidal particles (SCP-metal; < 0.2 µm), first described by Lombi et al. (2003), was undertaken. Analytical grade Na-Chelex-100 resin (Bio-Rad laboratories, UK) was converted to the Ca^{2+} form by equilibrating in 0.5 M $Ca(NO_3)_2$ for 2 hours. The resin was then washed twice with MilliQ water (18.2 MΩ cm) to remove remaining Na^+ ions. An aliquot of Ca-Chelex resin (c. 100 mg) was introduced into 10 mL of filtered (< 0.2 µm) solution from both spiked and un-spiked soil suspensions. After equilibration for 2 hours, the resin was rinsed with MilliQ water three times to remove colloidal particles. Metals were then eluted from the resin with 0.5 M HNO_3 and the measured isotopic ratio used to calculate the labile pool (M_{Er}; mg kg^{-1}). Results were compared with M_E measured directly on the filtered solution phase to test for the presence of non-labile SCP-metal.

Comparison with radio-labile metal fraction measured in October 1999

A comparison was made between values of Cd_E and Zn_E measured in this study in August and September 2011, and the 'radio-labile' fraction (M_E*) measured by Tye et al. (2003) on the same soils in October 1999 - shortly after collection of the Urban soils but following 818 d incubation at 80% field capacity in the case of the MA soils. The objective was to investigate possible further aging of Cd and Zn in MA and Urban soils following 12 years of soil storage under air dry conditions. In the study of Tye et al., the radio-isotopes ^{109}Cd and ^{65}Zn were used to determine Cd_E^* and Zn_E^*.

2.4 Analysis of soil solution

Elemental concentrations of dissolved major (Al, Ca, K, Mg and Na) and trace (Cd, Cu, Ni, Pb and Zn) cations were measured in 0.01 M $Ca(NO_3)_2$ suspensions with 1 g soil in 30 mL solution using ICP-MS, as described in Section 2.2. Dissolved organic carbon (DOC) and inorganic carbon (DIC) were determined in the suspensions using a Shimadzu TOC-Vcp analyser. For modelling purposes, an estimate of FA concentration in solution was made assuming that dissolved organic matter (DOM) contains 50% C and that 65% of DOM consists of active FA (Buekers et al., 2008b; Cheng et al., 2005).

2.5 Describing lability (%M_E) as a function of soil properties

Two types of empirical model for predicting $\%M_E$ from measured soil properties were assessed. The first was a multiple linear regression model where the simplicity of the equation allows inclusion of a large number of variables. Values of $\%M_E$ were correlated with a range of soil characteristics including pH, %SOC, %Clay, Al, Fe and Mn oxide contents (mg kg^{-1}) and total Cd, Cu, Ni, Pb, Zn concentration (M_{total}; mg kg^{-1}). The significance of each variable was determined (Minitab vs 16.2.2) and only those that were significant ($p < 0.05$) in predicting $\%M_E$ were included in the model (**Eq. 3**). The constants were optimized using the *Solver* function in Microsoft Excel.

$$\%M_E = k_0 + k_1\,(pH) + k_2\,(\%SOC) + k_3\,(FeOx) + k_4\,(MnOx) + k_5\,(AlOx) + k_6\,(\%Clay) + k_7\,(M_{total}) \quad (3)$$

The second model was a logistic (sigmoid) equation based on the assumption that pH is likely to be the primary determinant of $\%M_E$ (**Eq. 4**). A similar function has been shown to describe trace metal *adsorption* on soil binding phases (Sinitsyn et al., 2000; Lamy et al., 1993). Metal lability was therefore predicted assuming that $\%M_E$ was controlled only by pH and that the pH at which 50% of the metal was labile (pH_{50}) was metal specific (**Eq. 4**).

$$\%M_E = \frac{100}{1+exp[k_M(pH-pH_{50})]} \quad (4)$$

In **Eq. 4**, the 'spreading factor' (k_M) controls the slope of the model trend across the pH range and is probably unique to a particular soil-metal combination. Therefore, an attempt was made to refine **Eq. 4** by making k_M a function of other soil characteristics (S) describing the role of likely metal adsorbents (e.g. %SOC, metal oxide concentration and clay content); a power function (n) was added because it achieved a better fit to the data in practice (**Eq. 5**).

$$\%M_E = \frac{100}{1+exp[k_M S^n (pH - pH_{50})]} \quad (5)$$

A further simplification was to combine the measured oxide phases into a single variable, allowing for differences in the molecular weight for Al_2O_3, $Fe_2O_3 \cdot H_2O$ and MnO_2, resulting in three variables (%SOC, mineral (hydr)oxides and clay). Only one of the three variables was assumed to control the spread of $\%M_E$ values with pH (**Eq. 5**) for each metal. The constants in **Equations 4** and **5** were optimized, using the *Solver* function in Microsoft Excel, to assess the performance of each model.

2.6 Predicting trace metal solubility and speciation by WHAM-VII

The geochemical speciation model WHAM-VII was used to predict Cd, Cu, Ni, Pb and Zn concentration in the solution phase of soil suspensions. Measured values of M_E were used as inputs to WHAM, representing the total reactive trace metal fraction in the soil suspensions. The modelled metal concentration in solution was compared with measured values to assess the model performance. Speciation in solution and fractionation in the soil solid phase were derived from the model output. Model parameters and variables are listed in **Appendix 1**.

3. RESULTS

3.1 Soil characteristics

Full details of soil properties for the MA and Urban soils are provided as supplementary material (Appendices 2&3). Soil pH values covered a wide range, from < 4 to ~ 8; the Urban soils were slightly more alkaline with 60% of pH values > 6.0. All the soils can be categorized as mineral soils (%SOC < 20%) with two possible exceptions; Urban soils with 20.5% and 25.1% SOC, one sampled in a public park and the other near a railway line, both had evidence of coal in the soil. Urban soils from brownfield sites typically had the lowest %SOC (Appendix 2). Iron oxide content (FeOx) in both sets covered a wide range of values (5.4 - 43 g kg^{-1}); concentrations of Mn oxides (MnOx) were much lower than FeOx (0.16 – 3.01 g kg^{-1}), but the two variables were strongly correlated ($p < 0.01$). Iron oxides strongly adsorb trace metals at neutral and high pH values (Tack, 2010) whereas Mn oxides are more important at lower pH values due to their lower pzc (Dong et al., 2003; Trivedi and Axe, 2001). For the MA soils, uniformly amended with five trace metals, there was a relatively small variation in total metal concentration resulting from native soil metal content (Tye et al., 2003; Tye et al., 2004). Total metal concentrations in the Urban soils covered a much wider range as a consequence of historical contamination. Some individual metal concentrations in Urban soils were strongly correlated implying contamination from the same source (p-values < 0.05). Copper, Ni, Pb and Zn concentrations were positively, but weakly, correlated with %SOC (r_{Cu}=0.36, r_{Ni}=0.40, r_{Pb}=0.45, r_{Zn}=0.43,), FeOx (r_{Cu}=0.47, r_{Ni}=0.41, r_{Pb}=0.37, r_{Zn}=0.43) and MnOx (r_{Cu}=0.48, r_{Ni}=0.39, r_{Pb}=0.32, r_{Zn}=0.38) possibly as a result of their accumulation in soils with strong binding phases (Rieuwerts et al., 2006; Zimdahl and Skogerboe, 1977). Cadmium concentration was less affected by soil properties, only showing a very weak correlation with AlOx (r_{Cd}=0.34).

3.2 Measured metal lability in soils

Values of $\%M_E$ for Cd, Cu, Ni, Pb and Zn are shown in **Fig. 1**. For Urban soils the average $\%M_E$ values were 47.2% (Cd), 20.5% (Cu), 6.28% (Ni), 21.1% (Pb) and 18.1% (Zn) emphasising the need to consider metal lability (i.e. M_E, mg kg^{-1}), rather than just total soil metal content, when assessing risk and mobility in brownfield sites. Values of metal lability in the MA soils were significantly greater than in the Urban soils with average $\%M_E$ values of 74.4% (Cd), 48.7% (Cu), 36.2% (Ni), 54.1% (Pb) and 41.5% (Zn) despite three years incubation of MA soils at 80% field capacity and a further 12 years of storage under air dry conditions. In both sets of soils, the relative lability of the five metals followed the same sequence (Cd > Pb ≥ Cu > Zn > Ni).

The presence of a non-labile fraction of metal in suspended colloidal particles (SCP-metal) in the submicron filtered (< 0.22 μm) supernatant solutions from the soil suspensions used to measure M_E values was investigated by comparing M_E and M_{Er} (**Appendix 3**). For most of the soils, SCP-metal had only a very small effect on measured E-values. There was a strong correlation between $\%M_E$ and $\%M_{Er}$ and an average difference of less than 2% for all five metals; a significant difference was only observed

for Cu in the soils investigated. The ratio of Cu_E : Cu_{Er} against soil pH and $\%Cu_E$ (**Fig. 2a & 2b**) clearly suggests the presence of SCP-Cu, despite filtration to < 0.22 μm, especially at low levels of $\%M_E$ and high pH values in the Urban soils.

3.3. Predicting metal lability from soil properties

The effects of soil properties on values of $\%M_E$ were described in two ways: a multiple-regression model, which has the advantage of being able to include many variables, and a simple logistic model with soil pH as the primary determining factor.

In the current study, seven variables were available to predict values of $\%M_E$ from **Eq. 3**. Metal lability in the Urban soils is likely to have been affected by factors other than soil properties, especially metal source characteristics. Therefore, **Eq. 3** was parameterized using data from the MA soils only in which the added metal was from a single, initially dissolved, source. The goodness of fitting was evaluated from the values of RSD and correlation co-efficient (r). A good level of prediction was achieved for Cd (r=0.92, RSD=6.3), Ni (r=0.97, RSD=5.85) and Zn (r=0.95, RSD=7.7), but Cu and Pb were less successfully modelled, with correlation co-efficient equals to 0.83 and 0.85 respectively. Soil pH was negatively correlated with $\%M_E$ for all five metals and accounted for the largest proportion of the total variance in $\%M_E$ in the MA soils: 63.2%, 25.5%, 73.1%, 53.3% and 66.1%, for Cd, Cu, Ni, Pb and Zn respectively. The optimized constants, RSD values and correlation co-efficients (r) are summarized in **Appendix 4**.

Although linear regression modelling can provide reasonable predictions of metal lability where $\%M_E$ is largely a function of soil characteristics and a single contaminant source predominates, as in the MA soils, the application of this model is limited to the range of data used to parameterise the model. Extending 'prediction' of lability outside this range can result in physically impossible outcomes in which modelled values of $\%M_E$ may be negative, or > 100%. By contrast, a sigmoidal model (**Eq. 4**) offers more realistic boundaries to model outcomes ($\%M_E$ = 0 ~ 100%). The sequence of optimized pH_{50} values was Cd > Pb > Cu > Zn > Ni, and covered nearly three pH units, in agreement with the expected order of metal lability. The exponential factor k_M is related to the range of pH values over which the major change in $\%M_E$ occurs. Inclusion of each of the adsorption phases (OM, oxides, and clay) was then used to try and refine prediction of $\%M_E$ according to **Eq. 5**. For Cd, Ni and Zn, the best prediction, lowest RSD and highest value of r, was achieved by including total oxide content within **Eq. 5** (S value) to control the spread of predicted $\%M_E$ values as a function of pH. For Cu and Pb, including total oxide content also improved prediction of $\%M_E$, but the lowest RSD was obtained by including clay and organic matter content respectively. Copper produced the lowest k_M value (0.16) and so only gradually undergoes transition from labile to a fixed state over a relatively large range of pH values, whereas Ni and Zn were labile over a more restricted range of pH values with k_M values equal to 0.76 and 0.72 respectively. The optimized values of pH_{50} and the exponential constant k_M in **Eq. 4 & 5**, together with the results of modelling for the MA soils are shown in **Appendix 5**.

3.4. Metal lability in MA and Urban soils solely as a function of soil pH

Measured values of $\%M_E$ for Cd, Cu, Ni, Pb and Zn in MA and Urban soils, as a function of pH value, are shown in **Fig. 3** with model lines derived from **Eq. 4**. In the MA soils, for all five metals, there was no obvious bias in model prediction across the pH range. Measured values of Cu lability were only weakly correlated with pH. Although Cd and Pb also showed a restricted range of $\%M_E$ values, lability exceeded 90% and 80%, respectively, below pH 4.0. Zinc and Ni in the MA soils both showed substantially greater variation in $\%M_E$ with pH compared to the other three metals. Only small and non-significant differences between predicted values of $\%M_E$ were achieved by substituting **Eq. 5** for **Eq. 4** ($p > 0.05$) which implies no advantage in considering an effect of geocolloidal adsorption phase in the sigmoidal equation. The values of pH_{50} optimized using **Eq. 4** were very similar to those for **Eq. 5** and followed the observed sequence of relative metal lability in soils (**Appendix 5**). The measured values for the Urban soils are shown for comparison with the MA soils in **Fig. 3**. Soil pH affected metal lability in the Urban soils with a trend qualitatively similar to that of the MA soils but $\%M_E$ values were greatly over-predicted by the model (**Eq. 4** parameterised using the MA soils) in all cases.

Possible source effects were investigated by calculating the deviation from the model line as a proportion (%) of the modelled E-value ($\%\Delta M_E$); the model being parameterized solely from the MA soils for each element. No correlation between $\%\Delta M_E$ and pH or %C was observed with the exception of Pb where a trend with pH was apparent ($r = 0.602$) suggesting either a pH effect on the *source* of Pb or a continuing effect of soil-metal contact time (greater for the Urban soils). Thus, overestimation of $\%M_E$ values for Pb was greater for soils with high pH and low metal lability.

3.5 Changes in Cd and Zn lability in air dried soils during storage

For the MA soils, a paired t-test showed that the difference between M_E and M_E^* measured using radio-isotopes by Tye et al. (2003) was significant for Zn ($p = 0.007$), but not for Cd ($p = 0.416$). However, for the Urban soils, there was a significant difference for both Zn and Cd ($p < 0.001$) with, generally, $\%M_E^* > \%M_E$ (**Fig. 4a**). It is notable, for example, that the difference between M_E and M_E^* was more pronounced in high pH soils than in acidic soils (**Fig. 4b**). However, only a very small difference between M_E and M_E^* was observed in MA soils; the average ratio $M_E : M_E^*$ was 0.93 and 1.00 for Zn and Cd respectively. In contrast, for the Urban soils the ratios were 0.71 and 0.69 for Zn and Cd.

3.6 WHAM-VII prediction of metal solubility and fractionation

The ability of the geochemical speciation model, WHAM-VII, to predict Cd, Cu, Ni, Pb and Zn concentration in solution is shown in **Fig. 5** as modelled against measured solubility on a $-\log_{10}$ scale (pM_{soln}). Values of M_E were input to the model to represent the reactive metal pool in the soil suspensions (Appendix 1). Overall WHAM-VII predicted trace metal solubility reasonably well for both sets of soils. The values of RSD were less than 1 (pM_{soln} unit) for all five metals although the

average absolute bias ($\Delta p(M_{soln})$) differed between metals. Summary of model outcomes comparing the measured and the predicted are provided in the Appendix 6.

Predictions of Cu, Ni, Cd and Zn solubility were only slightly better for MA soils than for the Urban soils but the difference for Pb was greater: r values for Pb were 0.96 and 0.78 for MA and Urban soils respectively. Among the five metals, the model gave the best prediction for Cd and Ni with relatively low scatter around the 1:1 line (RSD = 0.51 and 0.63 respectively) and a high correlation coefficient (r = 0.94 for both metals). The high RSD value for Zn (0.83) occurred because the model substantially overestimated the solution concentration for several Urban soils with high pH values (6.93 to 8.08) and very low Zn concentrations in solution. Prediction of Cu solubility was reasonably good (RSD = 0.45; r = 0.74) but with some Urban soil outliers. Lead solubility was most poorly predicted by WHAM-VII (RSD=0.64; r=0.85). However, splitting the Pb dataset between MA and Urban soils, it was clear that, although there was less average bias compared to the other metals, the poor correlation coefficient and large RSD value was due to the Urban soils (RSD = 0.73, r = 0.78, ΔpPb_{soln} = -0.08), whereas solubility for the MA soils was more accurately predicted although with very slightly greater bias (RSD = 0.35, r = 0.96, ΔpPb_{soln} = 0.11).

Trace metal fractionation in the solid phase is provided by WHAM-VII as an output. Therefore, metal adsorption on different binding phases was investigated by interrogation of the WHAM-VII output data to determine whether particularly large deviations between measured and predicted metal solubility were associated with predominant sorption on particular binding phases. Average fractionation was modelled using WHAM-VII and includes six particulate geocolloidal fractions and a single pool for the solution phase, including 'colloidal' (dissolved) fulvic acid. **Figure 6** illustrates the average proportions of *labile* Cd, Cu, Ni, Pb and Zn predicted to be held in different soil phases alongside with changes in metal lability as a function of soil pH for both MA and Urban soils, as a combined dataset. For all five metals, **Figure 6** suggests that the relative importance of Fe-oxides for metal binding increases with pH, whilst that of organic matter (HA and FA) decreases. The WHAM model predicted that, on average, 96% of the Pb was adsorbed on Fe and Mn oxides for the MA and Urban soils; Mn oxides were more important below pH 6.5. By contrast, organic matter was most important for Cu across the pH range studied. Non-specific adsorption of Cd, Ni and Zn on clay was only significant in soils with very low pH values (pH 3.5 – 4.5) and low organic matter contents - less than 2.3%, 2.4% and 2.1% respectively.

Various factors may affect WHAM model performance in predicting metal solubility including soil pH and solid binding phase. The influence of soil pH value on model performance was statistically significant for Cd, Cu, Ni and Zn ($p < 0.01$), but not for Pb. Overestimation of metal solubility (log scale) increased with soil pH to give a positive correlation coefficient between ΔpM_{soln} (i.e. bias between the predicted and measured solubility by WHAM on –log scale) and pH. For Cd, Ni and Zn, the bias (ΔpM_{soln}) observed seemed to be mainly associated with the (modelled) proportion of labile metal bound to Fe oxides—especially for Cd and Zn in the high pH range (positive correlation coefficient). In the

case of Cu, bias was affected by Cu binding to particulate Mn oxides, and HA and colloidal (solution phase) FA. There was less over-prediction of solubility with increase in the proportion of Cu bound with HA and greater over-prediction with binding to colloidal FA-Cu. Prediction bias for Pb was relatively unaffected by soil pH or by the proportion bound to either Fe or Mn oxides; the range of bias was greater for the Urban soils. Correlation (r) between ΔpM_{soln} and soil pH or percentage binding with an important particulate phase (FeOx, MnOx, AlOx, HA) or colloidal (dissolved) phase (FA) are presented in Appendix 7.

4. DISCUSSION

4.1 The effect of soil properties and metal source on metal lability

Greater metal lability in the MA soils (**Fig. 1**) may partly reflect different soil-metal contact times for the two soil datasets, but it seems very likely that the characteristics of the original metal source are also responsible for lowering the lability in Urban soils. A similar conclusion regarding Cd lability in field contaminated soils was also made by Degryse et al. (2004) comparing radio-labile Cd in soils sampled adjacent to a smelter and 'metal salt incubated soils' but with a much shorter period of incubation.

The relative lability of the five metals in both MA and Urban soils followed the sequence Cd > Pb ≥ Cu > Zn > Ni which agrees with the observations of Gabler et al., (2007) who measured the lability of these five metals on 115 unpolluted soil samples using a stable isotope dilution approach. In the MA soils, where metal ions were originally added in solution, the difference in lability of the five metals only partly reflects their expected rates of fixation into soil constituents, based on a negative correlation with ionic radius, i.e. Ni ≥ Cu > Zn > Cd ~ Pb (Degryse et al., 2009; Degryse et al., 2007). The relatively larger proportion of Zn and Ni fixed may have been due to substitution for Fe in oxyhydroxides (Buekers et al., 2008a; Manceau et al., 2000), a mechanism which is less likely for larger ions such as Cd and Pb (Buekers et al., 2008a; Xu et al., 2006). However, the lower lability of Pb compared to Cd may be due to Pb precipitation as pyromorphite in phosphate-rich soils (Dermatas et al., 2008). Copper is predominantly bound with organic matter which may result in a slightly higher lability compared to Zn sorbed *within* Fe oxides.

For Ni and Zn, a smaller range of lability was seen in the Urban soils than in the MA soils. This may be counter to expectation because the Urban soils had a larger range of metal contaminant sources and the *range* of soil pH values (a major determinant of $\%M_E$) in the MA and Urban soils were broadly similar (**Appendix 2**). However, the lower lability of metal sources in the Urban soils also probably acts to limit the range of $\%M_E$ values in comparison with the MA soils. A restricted range of low $\%M_E$ values have also been reported for Pb in calcareous minespoils soils (Degryse et al., 2004; Marzouk et al., 2013a) and for Cd and Zn in soils contaminated with smelter wastes (Degryse et al., 2004). However, the greater lability of Cd in the Urban soils, relative to other metals, does not necessarily indicate that

404 the original source of Cd was more soluble. It has been shown that Cd and Zn added to soil in identical
405 (isomorphically substituted) forms (e.g. sphalerite) nevertheless end up with quite different labilities
406 following prolonged exposure to soil processes (Marzouk et al., 2013a; Degryse et al., 2004).

407 ***4.2 Prediction of metal lability***

408 Poor prediction of $\%M_E$ for Cu and Pb compared to Cd, Ni and Zn (**Appendix 4**) may arise from several
409 factors. It is widely recognised that adsorption on humus dominates Cu dynamics in soils (Weng et al.,
410 2001) but no significant correlation was found between Cu lability and %SOC in this study ($p > 0.05$).
411 Another possible explanation is a failure to include factors which might promote strong Cu binding
412 phases in the model, such as sulphide content (Du Laing et al., 2009). In some soils Pb is likely to
413 precipitate in non-labile mineral forms such as chloropyromorphite ($Pb_5(PO_4)_3Cl$) (Lang and
414 Kaupenjohann, 2003); fractionation of Pb in soils is generally less well described by current
415 geochemical models (Gustafsson et al., 2011).

416 The importance of pH as a predictor of lability (**Appendix 4**) is in agreement with previous studies
417 (Rieuwerts et al., 2006; Marzouk et al, 2013b). Stronger adsorption of metals is certainly expected with
418 increasing pH, partly due to the increase in negative charge on all adsorption surfaces. Metal *fixation* is
419 not necessarily linked directly to strength of adsorption, but it seems reasonable to assume that factors
420 that increase adsorption strength will also reduce isotopic exchangeability. Other processes may also
421 explain the influence of pH on lability, including preferential adsorption of metal hydroxide complexes
422 (Basta and Tabatabai, 1992) and precipitation as carbonate phases, (e.g. Gambrell, 1994; Charlatchka
423 and Cambier, 2000). In calcareous soils, diffusion into carbonate minerals (Hamon et al., 2002; Collins
424 et al., 2003; Buekers et al., 2007; Ahmed et al., 2008), or surface precipitation reactions (Ma et al.,
425 2006b; Nazif et al, 2015) are important. The significance of individual soil properties in
426 predicting $\%M_E$ was metal-specific; a positive coefficient (**Eq. 3**) may suggest that the adsorbent holds
427 labile metal and a negative coefficient may indicate a source of metal fixation. Thus the addition of
428 FeOx improved the prediction for Ni and Zn possibly suggesting that an important mechanism for metal
429 fixation is diffusion into Fe oxide micropores (Jacquat et al., 2009; Manceau et al., 2000; Degryse et
430 al., 2011). Although MnOx was correlated with the lability of all five metals (**Appendix 4**), it explained
431 $\leq$ 0.4% of total variance in predicting $\%M_E$ for Cd, Ni and Zn. For Cu and Pb, MnOx was more
432 important, accounting for 4.8 and 8.2% of the total variance in $\%M_E$ with a negative coefficient, which
433 is in agreement with previous studies (Bonten et al., 2008; Weng et al., 2001). The contribution from
434 clay content was extremely limited; only a very small proportion of 'isotopically labile' trace metal ions
435 are normally exchangeable with a neutral alkali-earth salt (Nakhone and Young, 1993). The correlation
436 with clay content may reflect a general association with soil mineral geocolloid content, rather than
437 implying that Zn and Ni are fixed within alumino-silicate clay minerals. Nevertheless, specific
438 adsorption of Zn within hydroxyl-interlayered clays in acidic soils has been demonstrated by Degryse
439 et al. (2011). Finally, there was a negative correlation between total Cd, Ni amd Zn and content and

values of $\%M_E$, probably because the larger content of native metal in the Urban soils (especially Zn) was less labile than the (fixed amount of) metal ions added as soluble salts to the MA soils.

The logistic model performance was generally slightly poorer than the fit achieved with multiple linear regression (**Appendix 4** and **5)**. However, **Eq. 4** has parameters (pH_{50}; k_M) that are more clearly related to the mechanisms that control trace metal lability and provides extrapolative predictions that remain realistic. Therefore, the simple logistic equation, expressing $\%M_E$ solely as a function of pH, is perhaps a more robust model for predicting metal lability solely and more useful than regression coefficients for comparative purposes.

Over-prediction of $\%M_E$ values in the Urban soils compared to the MA soils probably reflects the characteristics of the contaminant source on metal lability. This conclusion is further supported in **Fig. 3** by the greater scatter of $\%M_E$ values for the Urban soils seen for Cu and Cd and perhaps also the flatter trend with pH seen for Ni and Zn in Urban soils suggesting a primary mineral source less affected by pH-dependent adsorption strength. In the Urban soils set, more than half of the high pH soils (> 6.5) were associated with old industrial sites, i.e. brownfield, wasteland, etc. (Appendix 2), where metals probably entered the soils in a relatively non-soluble form. Secondary formation of poorly soluble minerals in calcareous soils (Degryse, et al., 2009) or Pb minerals (e.g. cerussite or chloropyromorphite) would also contribute to the trend seen. For example, the average measured lability of Pb in two phosphate-rich sewage farm soils (NG14 & NG15, 13.8%) was much less than that predicted by the MA-parameterized model (50.0%) suggesting precipitation of Pb phosphate minerals either in the soil or during the processing of the sewage sludge. However, it was difficult to identify any specific effects of historical or current land use on lability as, for example, soils from 'brownfield sites' produced values of $\%M_E$ for Cu ranging from 5.6% – 30.5% (NG19 and NG18, Appendix 2).

No effect of pH on $\% \Delta M_E$ was identified for Ni or Zn. A potential explanation is that Ni in these soils may be mostly attributable to parent material; this is supported by the low total Ni concentrations found (mean = 38.5 mg kg^{-1}; SD = 18.4 mg kg^{-1}). Only two soils had substantially higher Ni concentrations (**Fig. 3**). These were both from a sewage farm (NG14 and NG15) and had the highest values of $\%Ni_E$ (34.4% and 42.9%, respectively), suggesting that Ni lability in the sludge was high and that the soil-contaminant interaction was closer to the behaviour seen in the MA soils. It has been suggested previously that metal lability can be more dependent on the characteristics of the sludge than properties of the soil (Stacey et al., 2001). For example immobilization of soft acids such as silver, by soft bases such as sulphide has been recognized in biosolids (Donner et al., 2015; Donner et al., 2013). This suggests that Ni, as an intermediate metal cation, will be more strongly held by carboxyl groups in the organic matter of the sludge and remain labile. In contrast to Ni, total Zn concentrations in the Urban soils (mean = 283 mg kg^{-1}; SD = 178 mg kg^{-1}) were generally higher than in most soils in England and Wales in which Zn is typically <100 mg kg^{-1} unless contaminated by minespoil (Rawlins et al., 2012). Therefore it can be assumed that the Urban soils received Zn from sources other than parent material.

It is difficult to summarize the effect of land use on metal lability for the whole dataset because of the complex range of Zn sources. For example, from field notes, metals in soil WV20 were probably associated with canal dredgings whereas soil WV25 was contaminated from its location in an industrial estate and proximity to a railway - but both soils had similar values of $\%Zn_E$ (27.7% and 20.6% respectively). There was only one sample where Zn lability was, unexpectedly, underestimated by the MA-parameterized model and fell slightly outside of the RSD range: soil WV3 was a slightly acidic woodland soil (pH = 6.1) with very high DOC concentrations (180 mg L^{-1} in 0.01 M $CaCl_2$, 1g: 30 mL).

4.3 Aging of Cd and Zn in air dried soils during storage

The difference between values of M_E measured in the current study and M_E* measured by Tye et al. (2003) for Cd and Zn may be a consequence of processes occurring within the soils or it may be the result of analytical artefacts in either of the two methods (**Fig. 4**). Only a limited number of studies have compared the measurement of metal lability using both radio-isotopes and stable isotopes. Sterckeman et al. (2009) compared Cd lability measured using ^{111}Cd (stable; M_E) and ^{109}Cd (radioactive; M_E*) and found that the results were equivalent but that M_E data were more repeatable. Considering the range of properties of the MA soils, continuing fixation of Zn may have occurred in some soils. Even in air-dried soils, particles may have thin films of surface hydration which could mean that the soil remains sufficiently chemically reactive to allow solid phase matrix- and surface-diffusion processes.

The greater difference between M_E and M_E* for the Urban soils was surprising as there was no expectation of measureable metal fixation during the 12 years of air dry storage prior to measurement of M_E in August and September 2011 whereas further slow fixation in the MA soils was expected. This result may indicate a methodological difference. Values of M_E* were determined using flame-AAS and graphite furnace-AAS measurement of Cd and Zn combined with radio-assay of ^{109}Cd and ^{65}Zn in solution following centrifugation of soil suspensions at 2200 g. Values of M_E were determined solely by ICP-MS following additional filtration to < 0.22 μm. Thus, the (large) values of M_E* measured in 1999 may have been more susceptible to the influence of non-labile metal in suspended submicron particles (Lombi et al., 2003) - an effect which is enhanced at (i) higher pH values, (ii) lower soluble metal concentrations and (iii) lower values of $\%M_E$ - which are all characteristics of the Urban soils.

4.4 Effect of non-labile soil colloidal particles on measured E-value

A strong correlation between $\%M_E$ and $\%M_{Er}$ was expected because as metal lability increases there is less scope for a substantial effect from non-labile SCP-metal as M_{Er} gradually approaches the value of M_E at 100% lability. The increase in Cu_E/Cu_{Er} with pH (**Fig. 2b**) is in agreement with previous explanations of more mobile geocolloidal particles in the soil solution at higher pH values (Lombi et al., 2003; Nolan et al., 2009; Marzouk et al., 2013b). The presence of non-labile soluble Cu has also been shown to arise from strong adsorption of Cu on humic acid (Mao et al., 2015) whereas other trace metal ions (Cd, Ni, Pb and Zn) are more likely to be associated with colloidal Fe, Al and Mn oxides (Lombi et al., 2003; Ma et al., 2006a; Nolan et al., 2009). However, in this work no significant

correlation ($p > 0.05$) was observed between the ratio of M_E:M_{Er} and solution concentration of Fe, Al, Mn or DOC measured in 0.01 M $Ca(NO_3)_2$ (solid: solution ratio 1 g : 30 mL).

4.5 Prediction of metal solubility and fractionation with WHAM-VII

Metal binding

For all five metals the relative importance of Fe-oxides for metal binding appeared to increase with increasing pH whilst that of organic matter (HA and FA) decreased (**Fig. 6**). The pH-dependency of metal adsorption to Fe oxide is stronger than that of organic matter (Weng et al., 2004) and Fe oxide appeared to control metal binding at high pH (> pH 7), except in the case of Cu where organic matter was most important. Most of the Cu (> 91.0%) and Pb (> 92.3%) were absorbed by the soil across the pH range, even at low pH values, although there were substantial differences in their affinity for particular binding phases.

Errors associated with modelling

Errors in prediction of metal solubility may arise for reasons originating in both modelling and measurement. Model shortcomings may include poor parameterisation of the 'pure' geocolloidal metal binding parameters and failure to include all binding phases. The default constants in WHAM were originally parameterized on single geocolloidal systems and the most comprehensive datasets used in the sub-model employed (Model VII) were from studies of metal binding by purified humic and fulvic acids. Therefore it is likely that soils in which humus is the dominant adsorption surface are likely to perform better than those with complex assemblages of organic and mineral geocolloids. As suggested by Smith et al. (2004) the properties of the cation binding sites of humic substances in peat appear very similar to those of isolated humic substances. It has also been shown in other studies that prediction of the trace metal solubility with multi-surface geochemical models is more successful when solid ⇌ solution partitioning is controlled mainly by soil organic matter (Weng et al., 2002; Cances et al., 2003).

In contrast to Model VII for HA and FA, the surface complexation model for describing metal speciation on mineral oxides may be less rigorous in (i) combining all soil oxide adsorbents into just three types (Al, Mn and Fe oxides) and (ii) using a single parameter to describe heterogeneity for all metals (Lofts and Tipping, 1998) and oxides (default setting). Such simplifications are reasonable to avoid the need for a large parameter database limiting the applicability of the model. However, it may also be the reason for greater deviation from measured values in predicting solubility in high pH soils in which oxides are the dominant metal binding phases. Soils will have a range of oxide minerals, which vary in surface charge characteristics, surface morphology/area, crystallinity and degree of surface contamination with adsorbed anions and humus acids. All of these factors together will generate a range of adsorption strengths for metal cations. As pH rises, a greater range of metal oxides contribute to cation binding and so the *diversity* of oxide surfaces involved in metal adsorption will increase. Therefore, if a speciation model generates error in predicting metal binding on oxides surfaces, the effect is likely to be more significant in high pH soils as there is an accumulation of error contributed

by each oxide phase. In addition, there are other binding phases in soils which may actively adsorb metal cations especially in high pH soils. For example, calcite ($CaCO_3$) and hydroxyapatite ($Ca_5(PO_4)_3(OH)$), which are only likely to be present in soils with high pH (> 7.0 and > 6.0 respectively), can adsorb metal cations by surface replacement of Ca^{2+} on mineral surface sites (Davis et al., 1987; Ahmed et al., 2008; Bailey et al., 2005). The exclusion of these phases in the WHAM model may contribute to the general over-prediction of solution metal concentration at high pH. Alternative explanations offered within the literature include a failure to account for (i) synergistic effects associated with adsorption on mixed oxide-humic surfaces (Heidmann et al., 2005; Pedrot, et al., 2009); (ii) the existence of highly specific sites on Fe oxides with much greater intrinsic stability constants than used in the general surface complexation model (Buekers et al., 2008b; Linde et al., 2007) or (iii) formation of discrete solid phases such as chloropyromorphite ($Pb_5(PO_4)_3Cl$) (Degryse et al., 2009), which is likely to affect Pb dynamics in some of the Urban and sewage sludged soils.

Errors associated with measurement

Reasons for over-estimation and scatter in predicted solubility may lie not only with model limitations but also with the measurements undertaken to provide model inputs. Using reactive trace metal concentrations based on M_E values instead of 'total' improves the model prediction (Marzouk et al., 2013b). However, poor model input data is also likely to arise from the various 'proxies' that are used to represent geocolloidal binding phases. For example soil organic carbon is typically used to estimate soil humic and fulvic acid while the Fe, Al and Mn oxide phases are rather crudely represented by elemental extraction with a reducing reagent such as dithionite-citrate-bicarbonate solution. A significant underestimation of measured solubility (> RSD) was seen for a small number of soils (e.g. WV7 for Ni, Cu and Pb; WV10 for Pb, **Figure 5**). This may be a result of overestimation of some of the binding phases. For example, for soil WV7, WHAM predicted 70%, 83% and 97% of binding on Fe oxides for Cu, Ni and Pb, and the bias was-1.62, -0.83, and -2.25 respectively; this implies over prediction of metal binding on Fe oxides. Given that generally the model algorithms *underestimate* metal binding on mineral oxides, overestimation of metal binding suggests that, for these soils, the DCB method extracted more Fe than was actually present in the Fe oxides phase, leading to an overestimation of the Fe oxide content.

Bias in prediction of metal solubility in Urban soils

WHAM prediction of solubility in Urban soils generally produced a poorer correlation than that for MA soils. This may be the result of slightly higher pH values in Urban soils as a consequence of the presence of alkaline wastes such as cement, concrete etc. (Bridges, 1991; Rosenbaum et al., 2003). The higher metal sorption capacity seen in some brownfield soils, compared to non-urban soils, is thought to involve processes of both sorption and precipitation (Markiewiez-Patkowska et al., 2005; Mclean and Bledsoe, 1992). Some particular examples include (i) a large bias (ΔpM) observed for Zn and Pb with values of 1.7 and 1.8 respectively in soil WV21; (ii) extremely low metal solution concentrations which lead to greater experimental error in some urban soils - e.g. Zn in NG13 with pH 7.0 and total Zn

concentration 26 mg kg^{-1}; (iii) a very high binding capacity in sewage farm soils, possibly due to extremely high phosphate concentrations from the sewage sludge resulting in overestimation of Cd solution concentrations in NG14 and NG15.

5. CONCLUSIONS

For all five metals, lability in the MA soils was significantly greater than in the Urban soils, although the relative lability of the five metals followed the same sequence (Cd > Pb ≥ Cu > Zn > Ni) in both sets of soils. Lower metal lability in the Urban soils may reflect longer soil-metal contact times but also strongly suggests that metal source characteristics are more important. In the MA soils, a good prediction of %E-value was achieved using both linear and logistic models with pH value as clearly the most important soil property. Lability of Cu was least affected by soil properties. The addition of FeOx improved the prediction for Ni and Zn lability, while MnOx was important for Pb at pH values < 5.5. However, although the performance of the logistic model was no better than the linear one, it offers more realistic boundaries to model outcomes (%M_E = 0 – 100%) and is therefore perhaps a more robust model for predicting metal lability solely from soil properties and more useful than regression coefficients for comparative purposes. Soil pH affected metal lability in the Urban soils in a trend qualitatively similar to that of the MA soils. However, in all cases, the effect of contaminant source was evident from gross over-prediction of %E-value in Urban soils using logistic models parameterized with data from the MA soils. Continuing fixation of Cd and Zn may have occurred during soil storage. A more pronounced difference between M_E and M_E* was observed in high pH soils than in acidic soils. However, the difference between lability measured in 1999 and in the current study may also be due to the influence of non-labile SCP-metal in the earlier measurement.

Overall WHAM-VII predicted trace metal solubility reasonably well for both sets of soils and bias was observed mainly in soils with low metal solubility and relatively high soil pH values. For Cd, Ni and Zn, the bias observed was primarily associated with the proportion of labile metal predicted to bind to Fe oxides. In the case of Cu solubility, prediction bias was affected by Cu binding to particulate Mn oxides, and HA and colloidal (dissolved) FA. Of the five metals, Pb solubility was most poorly described. Solubility of all metals was predicted more accurately in the MA soils than in the Urban soils. This was likely to be the result of slightly higher pH values in the Urban soils or could indicate that the influence of metal source was not completely eliminated by using isotopically exchangeable metal as our best estimate of the labile metal pool required as input to WHAM VII. The poorer performance of WHAM-VII in predicting metal solubility in high pH soils may be the result of errors in modelling, including the exclusion of potential adsorption surfaces such as $CaCO_3$, or simplicity of the sub-model describing metal binding with mineral oxides. However there must also be considerable error associated with the simplistic representation of binding phases by measurement of ‘extractable’ Fe and bulk soil organic carbon.

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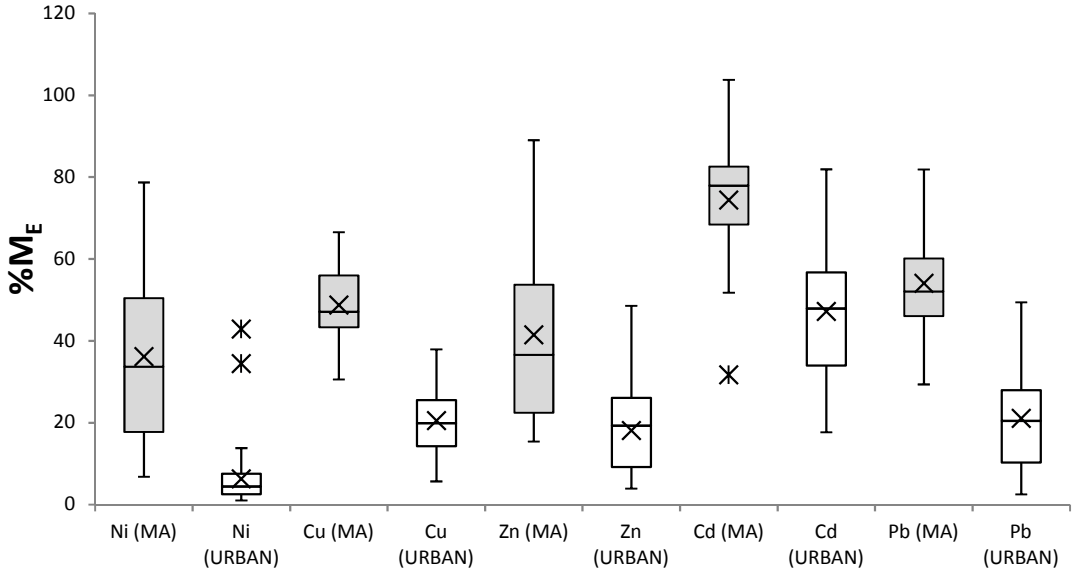

Figure 1: Box and whisker plot showing lability of Cd, Cu, Ni, Pb and Zn (% M_E) for MA soils (23) and Urban soils (50); the mean value (×) is also shown and outliers are marked as an asterisk.

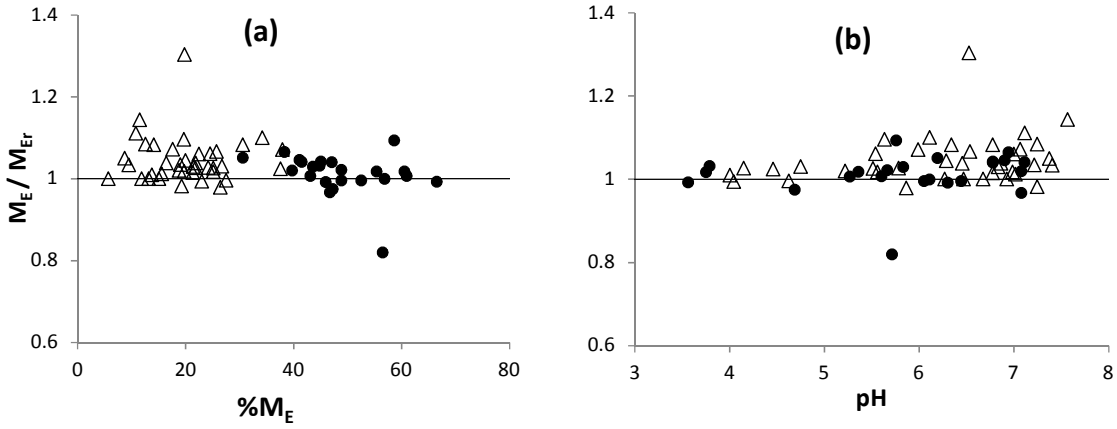

Figure 2: Ratio of M_E : M_{Er} as a function of $\%M_E$ (a) and pH (b) for Cu in MA (●) and Urban (Δ) soils.

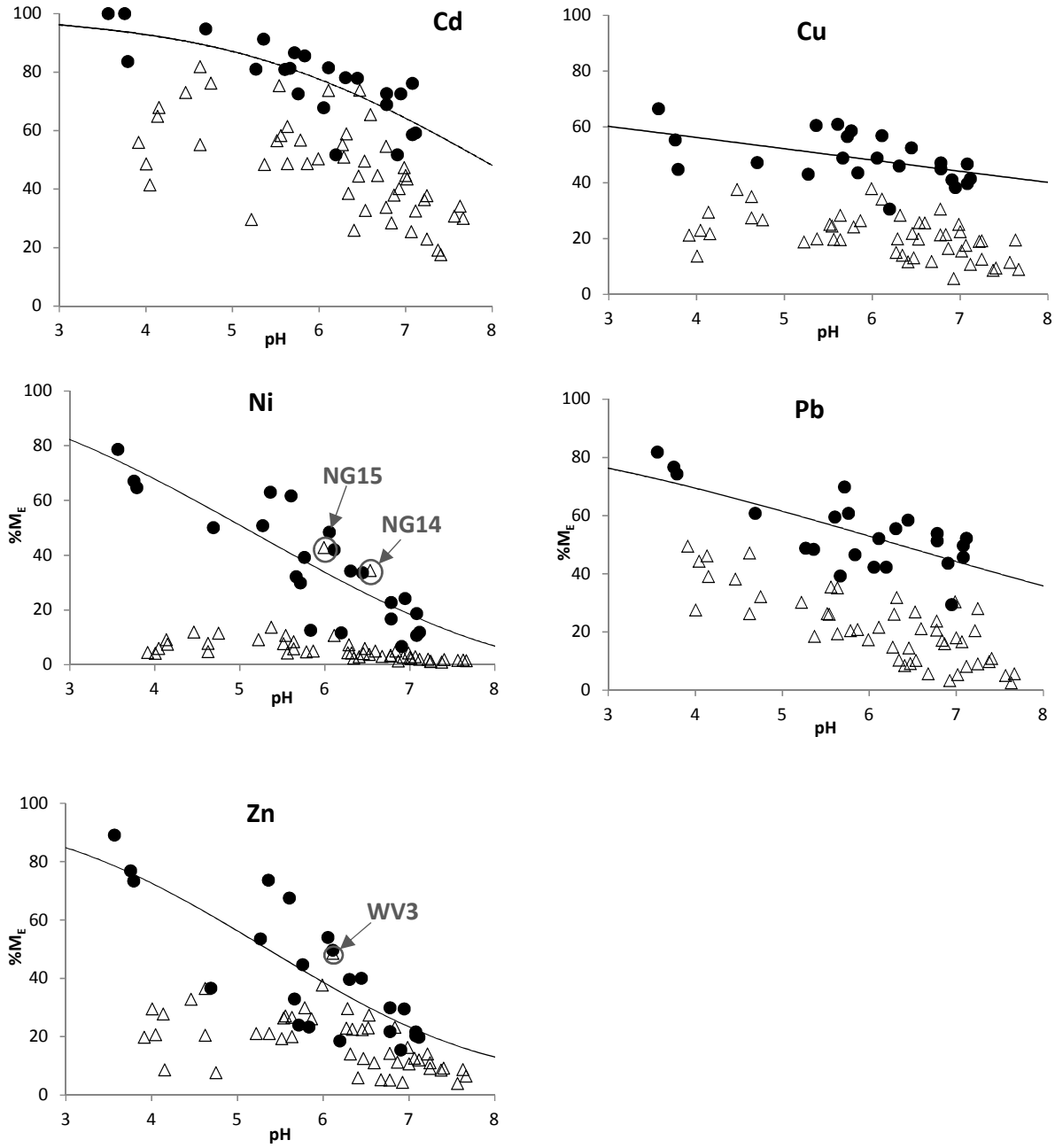

Figure 3: Measured values of $\%M_E$ (Cd, Cu, Ni, Pb and Zn) for MA (●) and Urban (Δ) soils. The solid line represents the predicted trend in $\%M_E$ from Equation 4.

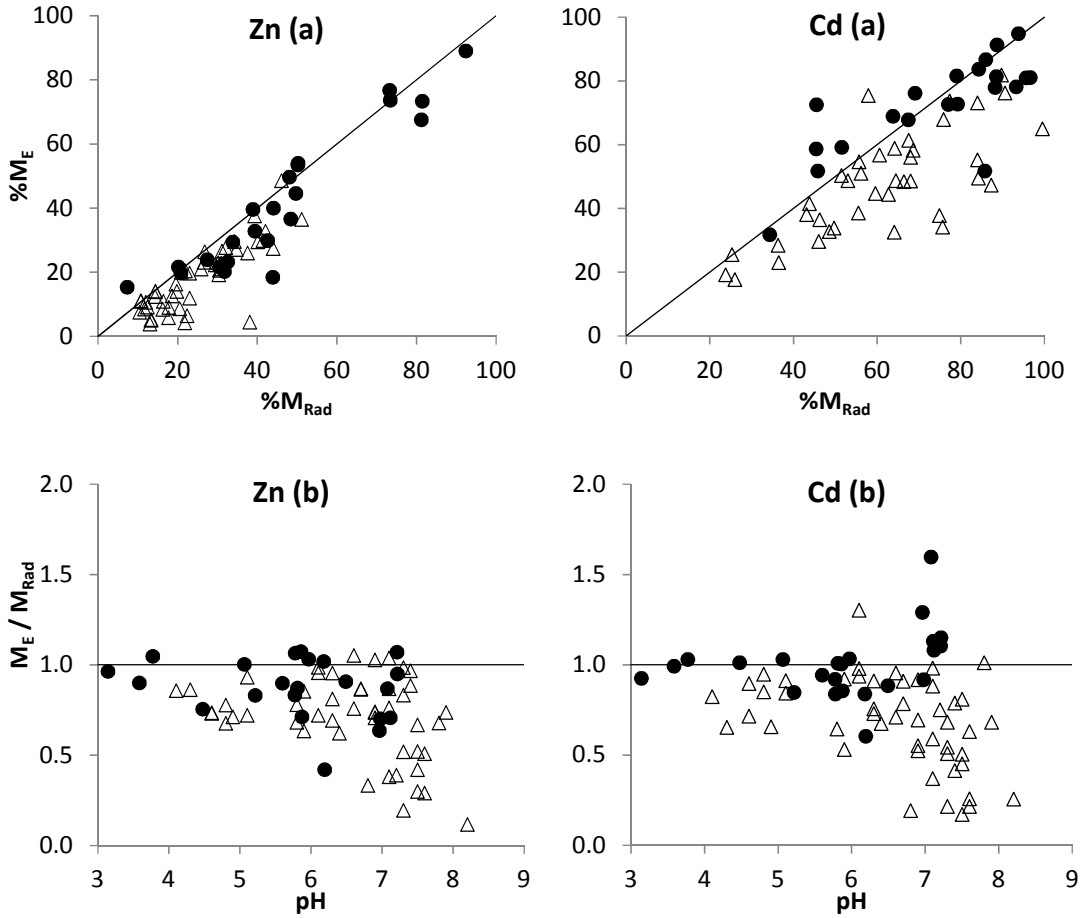

Figure 4: (a) Comparison of $\%M_E$ (this study) and $\%M_E$* (Tye et al., 2003) for Zn and Cd in MA (●) and Urban (Δ) soils; the solid line is the 1: 1 line. (b) The ratio of M_E : M_{Rad} as a function of pH.

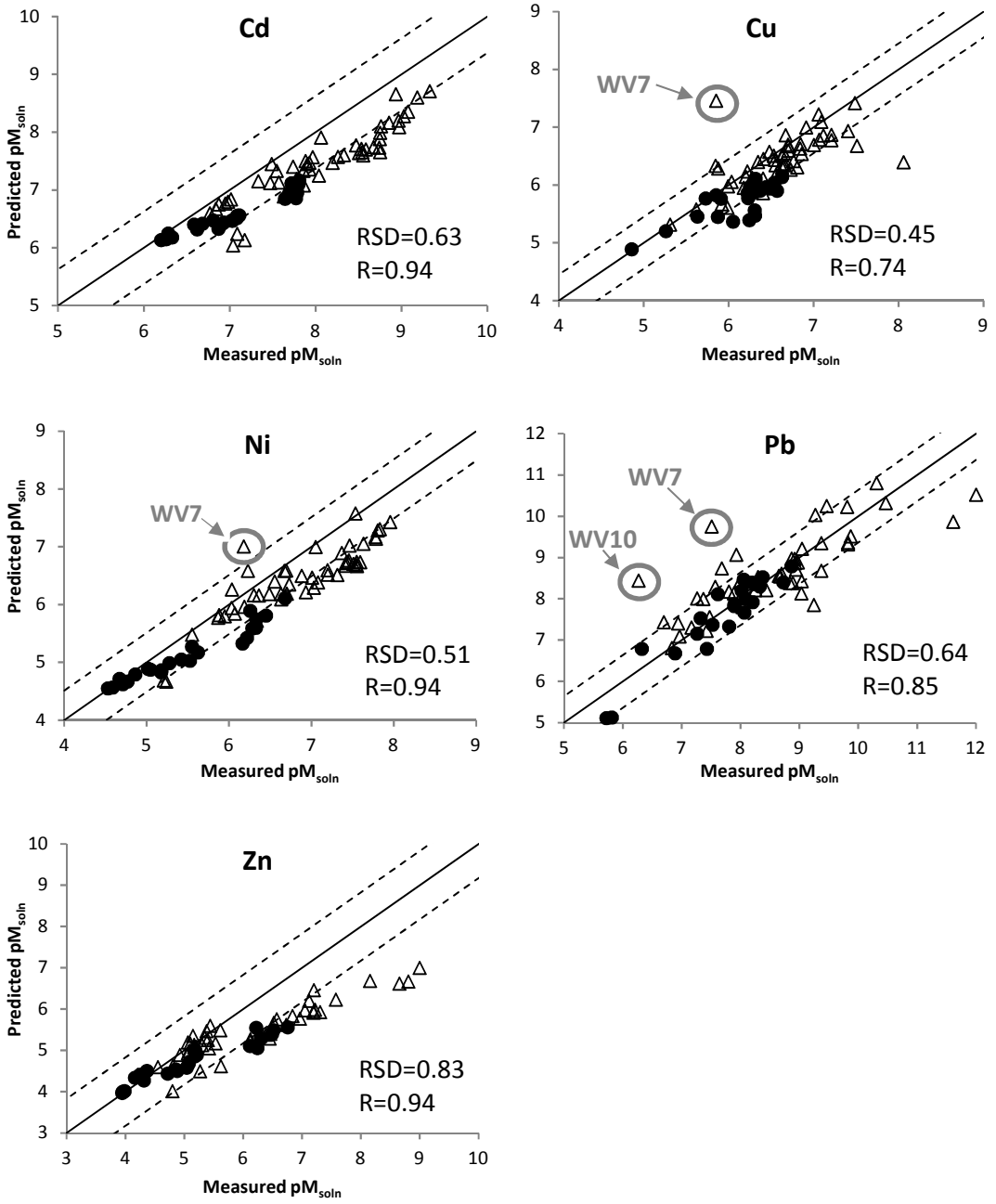

Figure 5: Solution concentrations ($pM_{soln} = -\log_{10}(M_{soln})$) of Cd, Cu, Ni, Pb and Zn predicted by WHAM-VII against measured values for MA (●) and Urban (Δ) soils suspended in 0.01 M $Ca(NO_3)_2$ (1 g: 30 mL). M_E was used as the input variable for reactive metal concentration. The solid line represents the 1:1 relation, and the dashed lines represent ± 1 RSD for the model. Values of RSD and correlation coefficients (r) are also shown.

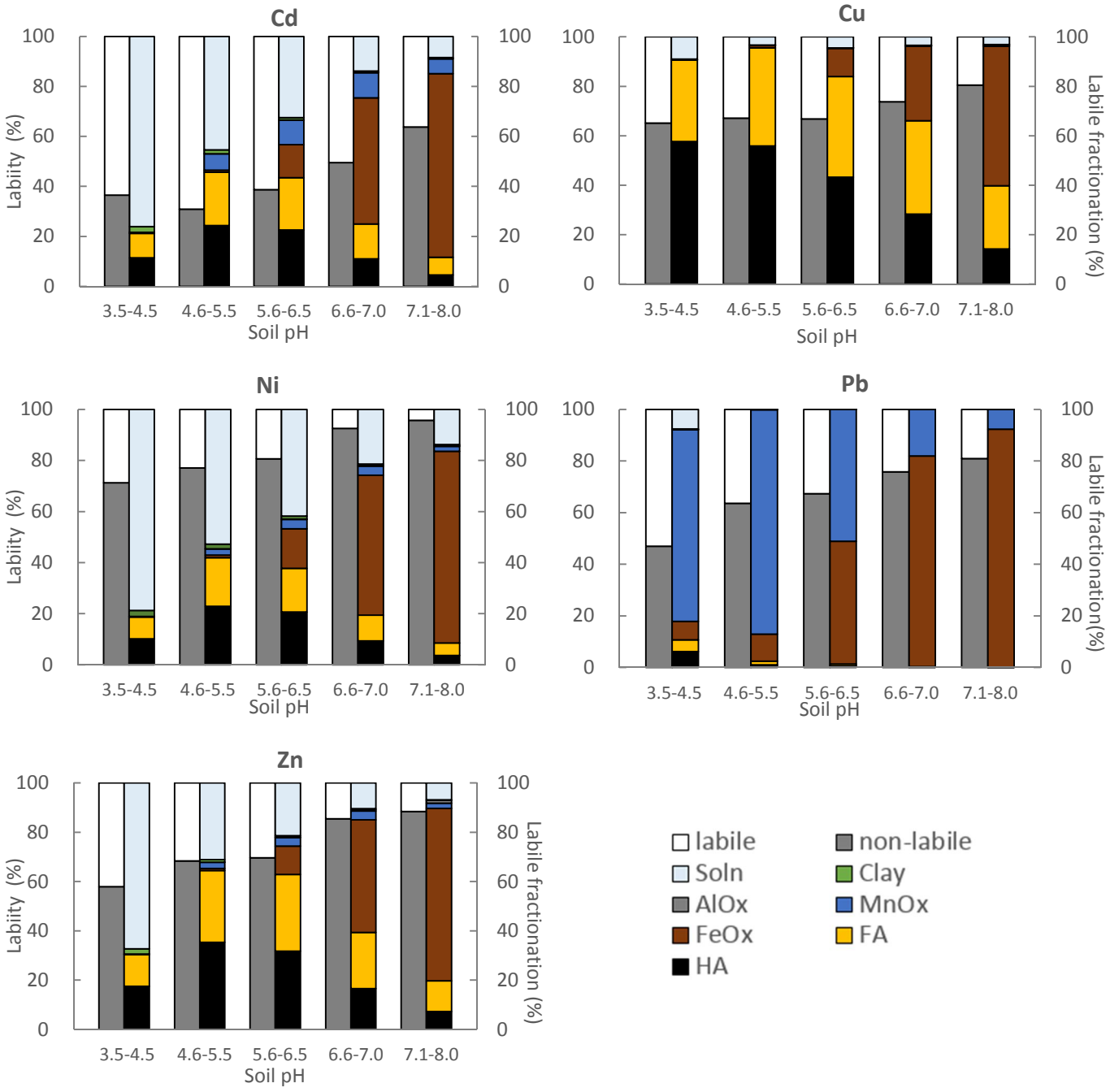

Figure 6：The first column shows fractionation by isotopic exchange into labile and non-labile metal (Cd, Cu, Ni, Pb and Zn) as a % of total soil metal content in MA (n=23) and Urban (n=50) soils, grouped by pH class. The second column shows the predicted distribution of the labile metal, only, between particulate humic and fulvic acid (HA and FA), Fe, Mn and Al oxides (FeOx, MnOx and AlOx), clays and the solution phase (Soln). Fractionation of labile metal was predicted using WHAM-VII parameterized using M_E as input (Appendix 1).

Appendix 1: Summary of the variables, parameters and settings for WHAM-VII modelling of trace metal solution concentration, speciation and fractionation.

Variable	Settings
Suspension condition	
Suspended particulate matter (SPM)	33.33 g L^{-1}
Temperature (K)	288.15 K (15°C)
PCO_2 (atm)	Measured bicarbonate concentration (DIC)
Soil pH	Measured in 0.01 M $Ca(NO_3)_2$ soil suspensions.
Charge balance options	No charge balance imposed i.e. a fixed (measured) pH value was used
Adsorption phase (g L^{-1})	
Clay content	MA soils: estimated from soil texture Urban soils: measured by laser granulometry
Fe, Al and Mn oxides	DCB extraction; converted to $Fe_2O_3.H_2O$, Al_2O_3 and MnO_2
Humic and fulvic acid	Measured by alkaline extraction
Colloidal fulvic acid	Estimated from measured DOC
Major cation and anion concentration (mol L^{-1})	
Dissolved major cations	Concentration in filtered soil suspensions (0.01 M $Ca(NO_3)_2$)
(Na, Mg, Al, K and Ca)	*Precipitation option for Al:* One mole of precipitated $Al(OH)_3$ forms 87 g of the binding phase within the particulate soil phase.
Fe^{3+} activity	*Precipitation option for Fe:* assumes that Fe^{3+} activity is controlled by $Fe(III)(OH)_3$ solubility, calculated within the model.
Dissolved nitrate (NO_3^-)	Solution concentration estimated as 0.02 M in the suspension
Total dissolved carbonate (all species)	Estimated from total inorganic carbon measured in solution
Trace reactive metal concentration in soil suspension (mol L^{-1})	
Total concentration Ni, Cu, Zn, Cd and Pb	Estimated from E-values (M_E)
Other settings	
Activity coefficient correction	Debye-Hückel
WHAM parameter data sets	Default master, solute and binding phase data bases.

Appendix 2 a): Summary of soil properties and total Ni, Cu, Zn, Cd and Pb concentration following metal amendment in MA soils.

Soil series*	pH	SOC	FeOx	MnOx	AlOx	Clay	Total Ni	Total Cu	Total Zn	Total Cd	Total Pb	DOC*
		%	g kg^{-1}	g kg^{-1}	g kg^{-1}	%	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg L^{-1}
Bardsey	3.57	3.18	19.9	0.16	1.44	35.0	69.6	134	273	2.5	343	48.1
Wick	3.76	4.47	17.9	0.22	1.26	10.0	82.1	158	327	2.7	346	58.1
Iveshead	3.79	6.55	16.3	0.20	2.99	5.0	73.8	147	328	3.1	345	46.0
Pwelliperian	4.69	3.03	14.6	0.47	3.44	35.0	97.7	161	498	3.1	341	26.0
Rivington	5.27	3.36	10.4	0.40	0.65	5.0	71.1	133	324	2.9	311	29.7
Braunshweig	5.36	2.28	5.4	0.61	0.10	15.0	73.3	138	318	2.8	292	18.0
Woburn	5.61	1.00	20.1	0.24	0.24	5.0	76.5	136	287	2.7	294	15.4
Fladbury	5.67	4.66	24.8	0.86	0.94	70.0	111	155	385	3.3	328	21.9
Ticknall	5.72	5.20	20.9	0.48	1.76	15.0	86.9	150	437	3.0	572	16.6
Cottam	5.76	2.08	15.6	0.61	0.67	15.0	92.1	161	365	3.5	332	12.9
Rosemaund	5.84	1.86	10.8	0.74	0.56	35.0	124	153	351	2.9	297	9.9
Arrow	6.06	2.08	15.9	0.57	0.64	10.0	83.1	156	347	3.2	323	10.3
Watlington	6.11	1.24	18.2	0.81	0.22	10.0	88.5	146	335	3.1	304	13.1
Insch	6.20	4.13	27.4	0.78	7.38	17.5	79.2	140	293	2.8	268	29.4
Newport	6.31	1.03	15.8	0.51	0.55	10.0	83.3	157	350	2.9	314	13.5
Gleadthorpe	6.45	1.68	8.8	0.35	0.41	10.0	75.2	145	341	3.0	306	13.8
Denchworth	6.78	4.42	18.9	0.77	1.07	70.0	98.0	155	316	2.8	300	10.8
Ragdale	6.78	4.10	29.8	0.79	1.60	35.0	107	154	404	3.3	321	13.3
Bridgets	6.91	2.38	28.7	2.68	3.01	35.0	108	142	377	4.3	306	7.1
Marian	6.95	7.06	15.8	2.54	0.15	35.0	93.6	172	417	3.2	377	16.3
Worcester	7.08	2.88	15.4	0.79	0.00	35.0	124	166	436	3.3	339	5.2
Hanslope	7.08	4.39	27.6	0.77	1.41	35.0	93.6	139	360	2.9	285	16.2
Evesham	7.12	2.38	22.0	0.98	1.11	70.0	97.6	155	337	3.0	312	7.6

*Soil Survey of England and Wales classification of soil series.

**DOC determined in suspension (1 g soil: 30 mL water).

Appendix 2 b): Summary of soil properties, sampling location, land use and total Ni, Cu, Zn, Cd and Pb concentration in Urban soils (Wolverhampton).

Sample	pH	SOC	FeOx	MnOx	AlOx	Clay	Total Ni	Total Cu	Total Zn	Total Cd	Total Pb	DOC*	Grid Ref.	Landuse
		%	g kg^{-1}	g kg^{-1}	g kg^{-1}	%	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg L^{-1}		
WV1	4.63	3.43	8.4	0.24	0.81	20.4	18.3	35.4	134	0.4	56.7	35.8	391030 301170	Grassland (golfcourse)
WV2	3.92	2.81	9.7	0.44	1.08	22.5	12.1	19.4	61.5	0.3	53.2	40.6	388450 300860	Grassland (golfcourse)
WV3	6.11	10.99	18.2	1.26	1.59	15.7	55.3	403	1050	3.7	266	59.4	393690 297700	Park
WV4	5.87	3.35	13.8	0.46	1.07	19.8	22.9	69.1	313	0.6	109	23.0	392180 297280	Grassland (open land)
WV5	6.46	13.28	26.3	0.84	1.16	14.6	77.9	233	588	1.3	227	8.0	393730 296530	Old industrial (gas works)
WV6	6.84	9.81	38.5	1.52	2.50	18.6	300	2200	4170	26.1	746	8.0	394490 295160	Wasteland (old landfill)
WV7	7.41	5.40	23.1	0.67	0.88	16.9	83.3	493	1170	3.6	590	3.2	394960 295960	Grassland
WV8	5.64	10.07	19.7	0.92	4.47	16.4	57.4	158	553	2.1	358	17.7	397060 296980	Woodland
WV9	5.56	4.39	16.8	0.62	1.66	18.4	32.3	134	300	0.9	273	17.5	390170 301290	Grassland
WV10	7.07	8.01	19.9	0.84	0.94	18.3	66.9	298	1100	4.1	1050	9.7	391330 301090	Old industrial (tyre factory)
WV11	4.46	3.68	14.9	0.38	1.80	22.9	25.3	87.7	514	1.9	173	28.9	390810 296710	Domestic garden
WV12	5.79	2.73	11.1	0.51	0.75	18.9	15.0	30.4	270	0.7	199	22.9	388240 295750	Grassland
WV13	5.54	3.83	12.6	0.64	0.71	24.4	25.4	51.1	308	1.0	131	22.1	392760 295760	Park
WV14	5.22	25.08	20.3	0.55	0.68	5.1	58.4	265	1190	5.1	332	16.2	392830 299710	Nature reserve (railway)
WV15	7.12	11.17	19.2	3.01	0.55	11.8	47.6	101	290	1.1	140	24.7	388910 299580	Nature reserve (railway)
WV16	4.01	14.46	7.1	0.27	5.10	16.8	29.1	89.1	135	0.7	88.4	18.0	392380 295460	Vegetated colliery spoil heap
WV17	5.64	2.76	11.1	0.52	0.87	19.4	26.9	73.8	239	0.6	141	50.3	391240 297580	Old industrial (disused factory)
WV18	4.63	5.49	16.7	0.51	2.49	22.6	39.8	204	524	1.7	150	26.3	395120 299290	Grassland (not maintained)
WV19	5.37	5.19	12.6	0.41	0.01	19.1	45.8	58.7	192	0.5	48.7	11.6	395150 299140	Grassland
WV20	4.14	4.54	10.8	0.25	2.36	15.3	15.1	77.6	105	0.5	85.7	30.4	396720 301130	Grassland
WV21	6.41	2.85	13.5	0.48	0.00	24.0	54.5	48.7	102	0.2	31.9	7.8	393960 299860	Brownfield
WV22	8.08	2.50	12.3	0.35	0.00	21.3	43.1	90.0	154	0.3	45.9	7.3	394390 299860	Brownfield
WV23	7.63	1.37	12.8	0.29	0.02	19.0	65.6	79.0	267	0.7	78.8	19.4	395400 299670	Brownfield
WV24	7.22	2.64	14.1	0.45	0.43	21.1	33.6	82.3	605	1.2	351	12.3	394680 299830	Brownfield
WV25	4.05	11.36	20.1	0.70	3.84	13.8	55.2	188	356	1.8	217	20.7	394210 298970	Grassland (park)
WV26	6.60	2.70	9.9	0.28	0.00	20.6	20.0	52.6	133	0.5	63.3	23.2	394600 298750	Grassland
WV27	7.67	3.16	28.7	0.54	0.29	20.5	39.1	160	279	0.6	177	15.3	392800 298520	Brownfield
WV28	7.25	5.85	21.1	0.44	0.66	18.8	44.8	150	281	0.6	156	10.6	391700 310630	Brownfield
WV29	6.87	20.50	27.4	1.03	0.64	20.0	94.1	338	739	3.3	429	10.4	391680 300080	Deciduous woodland
WV30	6.32	3.60	13.5	0.34	0.26	18.6	24.0	82.3	158	0.6	109	18.3	391780 300120	Grassland (park)

Appendix 2 c): Summary of soil properties, sampling location, land use and total Ni, Cu, Zn, Cd and Pb concentration in Urban soils (Nottingham).

Sample	pH	SOC	FeOx	MnOx	AlOx	Clay	Total Ni	Total Cu	Total Zn	Total Cd	Total Pb	DOC*	Grid Ref.	Landuse
		%	g kg^{-1}	g kg^{-1}	g kg^{-1}	%	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg L^{-1}		
NG1	4.75	5.00	40.6	1.67	3.81	24.6	49.5	51.4	340	1.8	194	29.9	455470 336660	Grassland (football field)
NG2	5.52	4.77	14.9	0.86	2.33	28.7	24.4	50.0	229	1.1	412	18.6	455280 338770	Churchyard
NG3	6.47	5.10	34.4	1.14	1.60	21.4	44.1	26.5	111	0.3	60.9	29.1	453760 341550	School
NG4	6.29	5.25	18.8	0.49	1.24	18.3	37.1	224	881	2.5	1300	7.0	454700 343720	Domestic garden
NG5	6.99	3.26	14.6	0.47	0.38	20.1	31.6	57.9	439	1.1	353	14.6	457360 342370	Domestic garden
NG6	6.78	10.70	39.5	0.81	1.36	19.8	60.1	161	459	2.0	406	14.6	458720 339210	Railway
NG7	7.00	5.31	21.4	0.85	0.88	18.8	59.0	129	359	1.5	385	13.0	458500 339110	Grassland (imported)
NG8	4.15	7.90	38.2	1.32	4.52	18.0	62.6	65.2	374	1.6	352	63.5	459710 339170	Grassland (racecourse)
NG9	6.27	4.81	14.6	0.38	1.50	20.5	28.2	47.6	169	0.6	205	14.5	453570 344310	Vegetated colliery spoil heap
NG10	6.53	5.21	18.5	0.79	1.38	21.7	35.2	54.4	301	0.8	257	11.7	455170 342480	Vegetated colliery spoil heap
NG11	7.25	8.56	25.3	1.30	1.83	14.8	228	1260	1690	2.1	1110	6.4	455770 338590	Disused factory
NG12	7.38	13.49	43.0	2.31	3.32	12.1	380	3190	2520	5.6	1240	6.9	455760 338550	Disused factory
NG13	7.02	1.28	15.6	0.35	0.03	20.7	20.3	26.0	26.0	0.1	18.5	8.0	453570 344210	Grassland (amenity)
NG14	6.54	11.41	16.7	0.59	3.59	13.0	370	644	1740	38.2	600	22.4	464120 340530	Sewage Farm
NG15	5.99	6.86	15.5	0.30	2.79	20.7	199	382	1020	19.2	337	21.1	464130 340810	Sewage Farm
NG16	7.57	5.03	25.0	0.93	0.61	18.9	44.0	92.9	223	0.9	121	7.3	462830 340800	Brownfield
NG17	6.34	18.25	27.7	1.06	1.33	11.6	99.0	274	634	1.1	1410	16.9	462770 340730	Brownfield
NG18	6.78	3.35	22.2	1.13	0.60	20.1	43.7	35.7	216	1.4	79.2	11.2	462900 340700	Brownfield
NG19	6.93	2.98	34.8	1.43	2.19	18.7	32.3	31.7	132	0.4	65.9	12.3	446800 339730	Brownfield
NG20	6.68	3.00	31.0	0.70	1.01	24.0	32.2	52.9	299	0.7	90.0	19.6	447040 339240	Brownfield

Appendix 3: Average difference between $\%M_E$ and $\%M_{Er}$ (ΔM_E), RSD, R^2, p-values for correlations between $\%M_E$ and $\%M_{Er}$ and standard error of the mean for replicate estimates of $\%M_E$ and $\%M_{Er}$.

	Ni	Cu	Zn	Cd	Pb
ΔM_E	-0.14	1.76	-0.52	-0.35	-1.59
RSD	0.79	4.84	28.22	0.13	15.49
r	0.999	0.997	0.973	0.997	0.963
p-value	>0.05	<0.01	>0.05	>0.05	>0.05
$SE_{\%ME}$	0.371	0.873	1.218	2.167	1.216
$SE_{\%MEr}$	0.468	0.666	0.636	1.189	1.854

Appendix 4: Linear regression model coefficients, RSD and r values for model prediction of $\%M_E$. The regression (see Eq. 3) was parameterized from $\%M_E$ (mg kg^{-1}) measured on MA soils. Values in brackets are the % of total variance, *n.s = not significant.*

	Constant	pH	%C	FeOx (g kg^{-1})	MnOx (g kg^{-1})	AlOx (g kg^{-1})	Clay (%)	Total metal content (mg kg^{-1})	RSD	r
Ni	176	-14.7**	-0.96	0.20*	0.90**	-4.42	0.02*	-0.55**	5.85	0.97
		(73.1)		(10.8)	(<0.10)		(<0.10)	(1.90)		
Cu	99.7	-4.87*	-1.20	0.38	-1.34*	-3.46*	-0.01	-0.13	5.20	0.83
		(25.5)			(4.80)	(24.7)				
Zn	180	-14.6**	0.53	0.04*	1.49**	-4.68	-0.19*	-0.13*	7.70	0.95
		(66.1)		(5.5)	(<0.10)		(<0.10)	(10.9)		
Cd	185	-11.5**	-0.39	0.12	3.10**	-3.39	0.06	-13.2**	6.30	0.92
		(63.2)			(0.40)			(7.70)		
Pb	75.9	-7.02**	-1.08	0.57	-7.26**	-0.76	-0.01	0.06	6.91	0.85
		(53.3)			(8.20)					

** significant ($p< 0.01$), * significant ($p< 0.05$)

Appendix 5: Values of model parameters (pH_{50}, k_M, n), RSD, r values and $\Delta\%M_E$ (average deviation of predicted $\%M_E$ from measured value) from sigmoidal model prediction of %E-value using Eq. 4 and Eq. 5 applied to MA soils only. The values in bold italic are the best fit of the measured $\%M_E$.

		Ni	Cu	Zn	Cd	Pb
Equation 4:						
	pH_{50}	5.06	5.55	5.36	7.89	6.33
	k_M	0.76	0.16	0.72	0.66	0.35
	RSD	11.5	7.59	13.2	8.73	8.97
	r	0.85	0.51	0.81	0.77	0.72
	$\Delta\%M_E$	-0.39	-0.01	0.01	0.13	0.12
Equation 5:						
pH + %SOC	**pH_{50}**	4.94	5.17	5.02	7.59	***6.27***
	k_M	0.54	0.07	0.23	0.38	***0.12***
	n	0.28	0.57	0.95	0.86	***0.86***
	RSD	11.2	7.66	13.3	11.5	***8.53***
	r	0.86	0.50	0.81	0.65	***0.76***
	$\Delta\%M_E$	0.18	0.66	1.43	0.37	***0.74***
pH + Ox	**pH_{50}**	***4.99***	5.47	***5.29***	***8.03***	6.40
	k_M	***0.16***	0.06	***0.12***	***1.19***	0.13
	n	***0.83***	0.57	***0.95***	***-0.40***	0.55
	RSD	***10.4***	7.45	***12.3***	***8.06***	8.80
	r	***0.88***	0.53	***0.84***	***0.81***	0.73
	$\Delta\%M_E$	***0.15***	0.40	***1.08***	***0.06***	-0.02
pH + %Clay	**pH_{50}**	5.01	***5.70***	5.16	7.22	6.46
	k_M	0.20	***0.03***	0.03	0.10	0.02
	n	0.41	***0.57***	0.95	0.86	0.86
	RSD	10.0	***7.17***	14.5	11.8	11.4
	r	0.89	***0.58***	0.77	0.65	0.51
	$\Delta\%M_E$	1.05	***0.12***	2.75	0.19	2.04

Appendix 6: Summary of model outcomes comparing predicted and measured solution concentrations of Ni, Cu, Zn, Cd and Pb using E-values (M_E) as input variables to WHAM-VII (Appendix 1; Fig. 5).

	Ni	Cu	Zn	Cd	Pb
RSD	0.51	0.45	0.83	0.63	0.64
r	0.94	0.74	0.94	0.94	0.85
Δp(M)	0.40	0.23	0.58	0.56	-0.02
slope	0.82	0.73	0.54	0.78	0.80
intercept	0.77	1.53	2.08	1.11	1.70

Appendix 7 a): Correlation (r) between ΔpM_{soln} (the bias between measured and modelled solubility by WHAM on a –log scale) and soil pH or percentage binding with an important particulate phase (FeOx, MnOx, AlOx, HA) or colloidal (dissolved) phase (FA).

r	Ni	Cu	Zn	Cd	Pb
pH (p<0.01)	0.431	0.354	0.751	0.749	
FeOx (p<0.05)	*0.284*		*0.744*	*0.532*	
MnOx (p<0.05)	*0.270*	*0.342*			
HA (p<0.05)		*-0.414*			
Colloidal-FA		*0.510*			

Appendix 7 b): Difference between measured and predicted Pb solubility (ΔpPbsoln) as a function of (a) soil pH and fractional sorption by (b) FeOx and (c) MnOx.